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CRLR 522
Projects 4-92-03-012
4-92-03-013-02

FORMAL REPORT

**PREPARATION AND PROPOSED SEMICONTINUOUS PROCESS
FOR PRODUCTION OF AGENT Q (U)**

by

Pfc. Manfred Lichtenstadter
Lt. James D. Moneymaker



FC

**CHEMICAL CORPS
CHEMICAL AND RADIOLOGICAL LABORATORIES
Army Chemical Center
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PREPARATION AND PROPOSED SEMICONTINUOUS PROCESS FOR PRODUCTION OF AGENT Q (U). - M. Lichtenstadter & J. Money-maker	
CRLR 522, 21 Mar 56, 36 pp - illus - tables (CONFIDENTIAL)	Project 4-92-03-012 and 4-92-03-013-02
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Army Chemical Center
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PREPARATION AND PROPOSED SEMICONTINUOUS PROCESS FOR PRODUCTION OF AGENT Q (U)

Submitted by:

Recommending approval:

* Manfred Lichtenstadter
*Pfc. Manfred Lichtenstadter

Gordon N. Jarman
Gordon N. Jarman
Chief, Chemical Process Branch

James D. Moneymaker
*Lt. James D. Moneymaker

M.G. Ringenberg
M.G. Ringenberg
Chief, Plants Division

William H. Manogue
William H. Manogue

APPROVED:

Sigmund R. Eckhaus
Sigmund R. Eckhaus

for Fred J. Delmore
FRED J. DELMORE
Colonel, CmlC
Commanding

*P-60 NM

*Author

Notebooks: 3956, 4408, 4477, 4431

Experimental work:

Started: October 1954
Completed: April 1955

Control no.
5022-522

Typed: 21 March 1956
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ABSTRACT

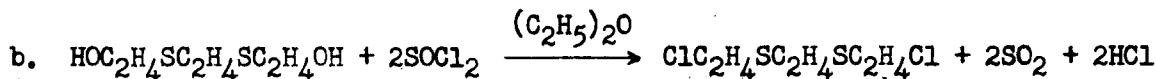
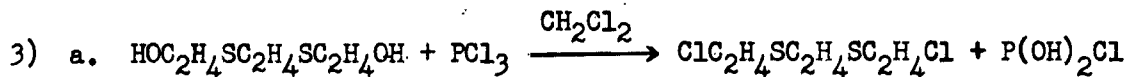
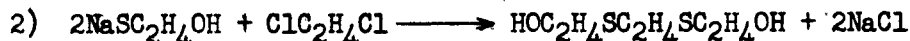
Object.

The object of project 4-92-03-013-02 (4-92-03-012) is to design, install, maintain, and operate the pilot-plant equipment and facilities used in connection with the development and manufacture of CW agents.

The object of the work described in this report was to develop a semicontinuous process for the manufacture of bis(2-chloroethylthio)ethane, agent Q, and to supply agent Q as required for testing.

Results.

Agent Q was prepared in the following manner:



Totals of 62.4 lb. of bis(2-hydroxyethylthio)ethane (sesquiglycol) and 48.2 lb. of agent Q were produced by these procedures.

Agent Q was prepared semicontinuously using phosphorus trichloride as a chlorinating agent and dichloromethane (methylene chloride) as a carrier for the sesquiglycol. Methylene chloride was used as the carrier because it can be used to extract sesquiglycol from the condensation-reaction mixture and can be easily stripped from the finished product.

A flow diagram and material balance for the proposed semicontinuous process is included in this report.

Conclusions.

Agent Q can be prepared in high purity and with high yields by using phosphorus trichloride to chlorinate a suspension of sesquiglycol in methylene chloride. A process to manufacture this agent semicontinuously has been developed so that no intermediate purification of sesquiglycol is required.

Recommendations.

It is recommended, if any future interest arises in this CW agent, that the process, as discussed in this report, be considered for pilot-plant operation.

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PREPARATION AND PROPOSED SEMICONTINUOUS PROCESS FOR PRODUCTION OF AGENT Q (U)

I. INTRODUCTION.

A. Object.

The object of project 4-92-03-013-02 (4-92-03-012) is to design, install, maintain, and operate the pilot-plant equipment and facilities used in connection with the development and manufacture of CW agents.

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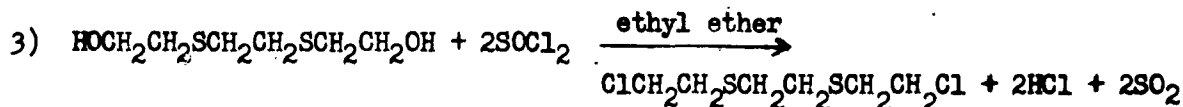
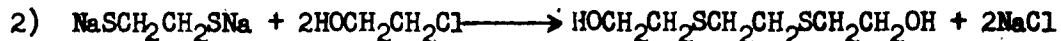
B. Authority.

The authority for this work was contained in the 1955 project program, Project 4-92-03-013-02 (4-92-03-012),* CW Agent Pilot Plants.

II. HISTORICAL AND THEORETICAL.

Several methods are available for the preparation of bis(2-chloroethylthio)ethane, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$, or agent Q. The preparation of the corresponding hydroxy compound, bis(2-hydroxyethylthio)ethane (sesquiglycol), and its chlorination in ethyl ether solution with thionyl chloride has been accomplished in the Chemical Process Laboratory (1).

Starting with 1,2-ethanedithiol and 2-chloroethanol, the agent was produced in the following manner:



The use of hydrochloric acid in the chlorination of sesquiglycol in aqueous solution was investigated by Preuss and Wardell (2). The resulting yields were poor, and the purity of agent Q was low.

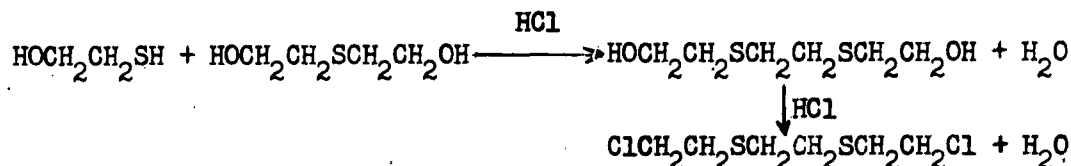
The preparation of agent Q by the photochemical addition of chloroethylene to 1,2-ethanedithiol has been reported, and the background on this method was included in the report by Eckhaus and DeWitt (1).

* Renumbered 9 December 1954 (CCTC item 2962).

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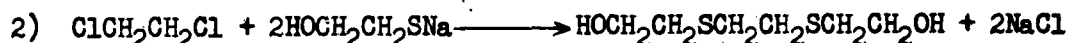
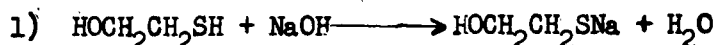
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A third procedure for the production of agent Q was the HQ process (3). This procedure involved the supposed condensation of 2,2'-thiodiethanol (thiodiglycol) and 2-mercaptoethanol, and inferred reaction of the condensate with hydrochloric acid as shown in the following reactions:



The optimum yield of agent Q was obtained when a weight ratio of 8.5 to 1.5 of thio alcohols was used. This gave a reaction mixture containing 20% to 35% of Q and 65% to 80% of H. Production of H, although not shown in the equations, can be readily understood. Increasing the amount of 2-mercaptoethanol did not increase the amount of Q in the reaction mixture, but homologs of this series of higher molecular weight were found. To recover the Q, the H was removed by vacuum distillation.

The hydroxy compound could be prepared by a method reported by Adams and Marvel (4). The reactions were as follows:



This material, prepared in this manner, could be chlorinated using the thionyl chloride method.

An investigation was initiated to find other agents and solvents for chlorinating sesquiglycol (5). It was reported that phosphorus trichloride (PCl_3) was successfully used to chlorinate sesquiglycol suspended in dichloromethane (methylene chloride) solution (6). This solvent could also be used to extract sesquiglycol from the Adams and Marvel (4) reaction mixture, thereby making a semicontinuous process for the preparation of agent Q feasible. Based on the preparation of sesquiglycol by the Adams and Marvel method, its extraction with methylene chloride, and its chlorination with phosphorus trichloride, efforts to develop a semicontinuous process were made.

III. EXPERIMENTAL.

A. Materials.

1. Sodium hydroxide (NaOH), Octagon Process, Inc., A.C.S. pellets, 97.0% purity.
2. Dichloromethane (methylene chloride, CH_2Cl_2), Belle Alkali Company, b.p. $40^\circ\text{--}41^\circ\text{C}$., density 1.336 g./ml.

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3. 1,2-Dichloroethane (ethylene dichloride, $\text{ClCH}_2\text{CH}_2\text{Cl}$), Carbide and Carbon Chemical Company, b.p. $83^\circ\text{--}84^\circ\text{C}$.

4. 2-Mercaptoethanol ($\text{SHCH}_2\text{CH}_2\text{OH}$), Carbide and Carbon Chemical Company.

5. Phosphorus trichloride, procured from Site A, Military Specification MIL-P-10398A (Cml C), 6 May 1952.

6. Thionyl chloride (SOCl_2), procured from Columbia Southern Chemical Company.

7. Ethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$), anhydrous, c.p., b.p. 34.5°C .

8. Methanol (CH_3OH), Carbide and Carbon Chemical Company, commercial grade, meets U. S. Army specifications.

9. Acetone (CH_3COCH_3), commercial grade.

B. Preparation of 1,2-Bis(2-hydroxyethylthio)ethane or Sesquiglycol.

1. Reaction.

A solution of 485 g. (12 moles) of sodium hydroxide in 2.5 l. of water was placed in a 5-l., three-necked flask equipped with a dropping funnel, reflux condenser, and an efficient stirrer. Then 945 g. (12 moles) of 2-mercaptoethanol was added slowly, with stirring, to the cooled alkali solution. As the 2-mercaptoethanol was added, the solution first turned green. The green color faded as the neutral point was reached and was replaced by a pink color on further addition of the 2-mercaptoethanol. The mixture was heated to 65°C ., and 620 g. (6.1 moles) of ethylene dichloride was added slowly, with efficient stirring, at such a rate as to keep the ethylene dichloride (b.p. 84°C .) refluxing. This addition required roughly 1 hr., and on completion, the mixture was heated to 85° to 90°C . for another hour to insure completion of the reaction. Agitation of the reaction mixture keeps the oil emulsified with the reactant mass. Fig. 1 shows the bench-scale setup.

2. Purification of Crude Reaction Product.

a. Adams and Marvel Procedures.

(1) Filtration. On completion of the reaction, the reaction mix was cooled, with stirring, with an ice bath until the product solidified. The product was collected on a filter, and the filtrate was cooled to obtain additional precipitate. When this procedure was attempted on a process scale, the entire reaction mix solidified, thereby making separation by filtration impossible.

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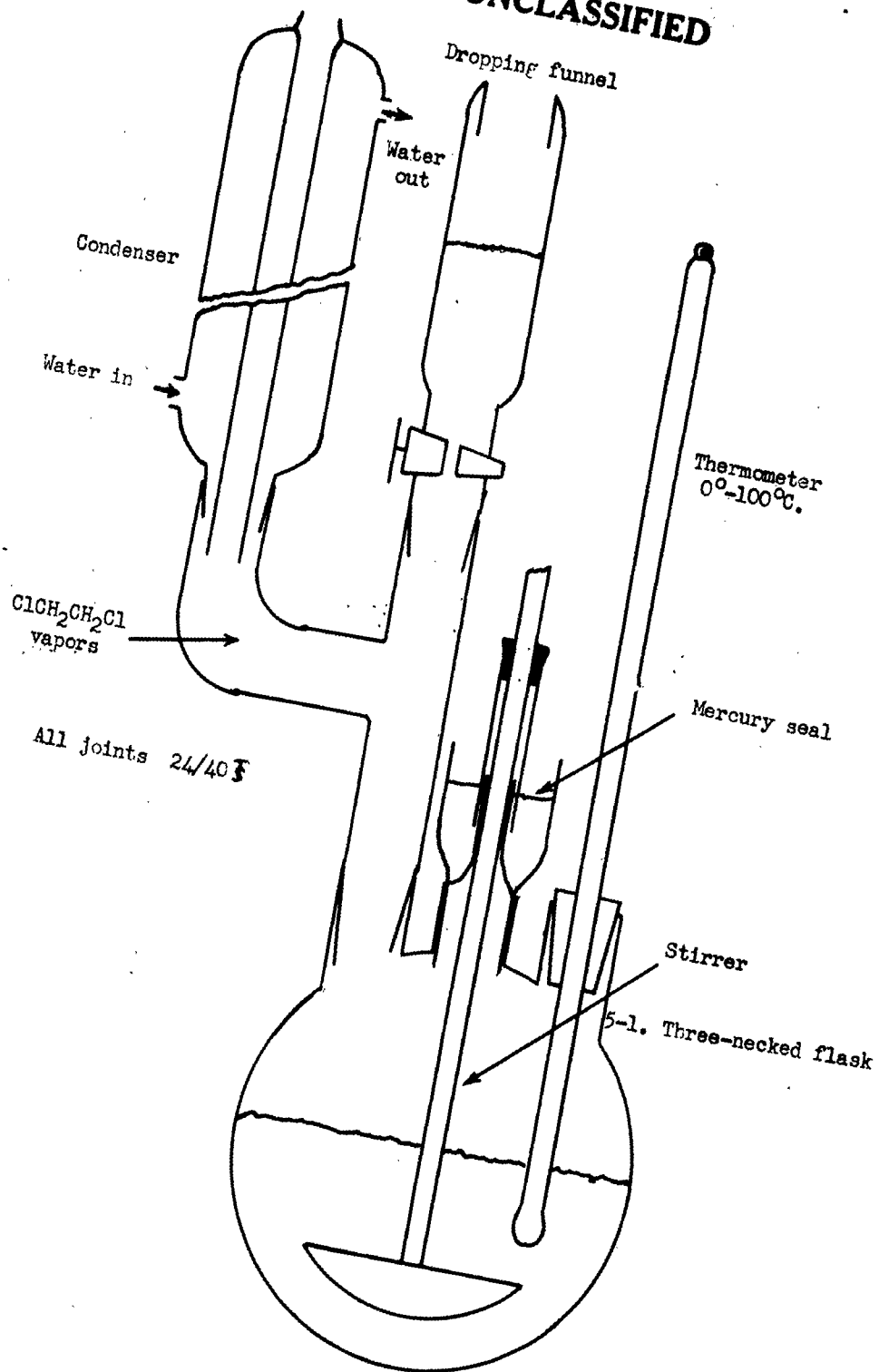


FIGURE 1

BENCH-SCALE REACTOR

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(2) Separation of Oil Layer. An alternate procedure suggested by Adams and Marvel was to separate the oil layer at 65°C. and then recover the remaining glycol from the aqueous layer by cooling and filtering.

Two runs, on one-tenth the scale described above, were made to check this procedure. Table 1, below, gives a complete breakdown of the two streams as calculated from chlorine analysis.

Table 1

Analysis of Product Streams on Separating at 65°C.

Run	Aqueous layer				Oil layer			
	Total reaction mix	Sesquiglycol	NaCl	H ₂ O	Total reaction mix	Sesquiglycol	NaCl	H ₂ O
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
2	74.0	9.2	19.2	71.6	26.0	71.2	5.0	23.8
3	78.3	8.9	21.1	70.0	21.7	69.2	3.0	27.8
3a*	78.3	11.5	18.5	70.0	21.7	69.9	2.3	27.8

* Based on sulfur analysis.

The results of these two runs are in fairly good agreement. A satisfactory check of the material balance was obtained on run 3, using the sulfur analysis. From table 1, it can be seen that the amount of water and NaCl in the oil layer makes direct chlorination of this material dispersed in a solvent undesirable. Impurities present would remain in the Q.

b. Process Laboratory Procedures.

(1) Removal of Water.

(a) Atmospheric Distillation. To remove water from the whole reaction mix, run 4 was distilled at atmospheric pressure. Pot temperatures during this distillation ranged from 106° to 110°C. while the vapor temperatures remained constant. Of the theoretical amount of water in the reaction mix, 97.6% was removed in this manner. The viscous, liquid residue turned yellowish brown. NaCl precipitated during the distillation. Acetone (200 ml.) was added to the reaction flask, and the mass was then filtered. The filtrate was dried to remove the acetone. A total of 105.8 g. (97.5% theoretical yield) of brownish product was recovered. This material had a strong mercaptan odor, indicating that the reaction did not go to completion (probably due to insufficient NaOH). Analysis of this material showed 0.0%

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chlorine and a melting range of 48.5° to 59°C., with some residue which did not melt at 134°C.

(b) Vacuum Distillation. To decrease possible product breakdown, runs were distilled under reduced pressure, thereby lowering the pot temperatures. In run 5, attempts to hold pot temperatures at 65°C. during the distillation failed, as constant boiling could not be maintained. The reaction mixture bumped vigorously on occasion and ejected an emulsion into the condenser. The pot temperature was raised to 80°C., and air was bled into the vacuum system. Distillation proceeded smoothly until NaCl began precipitating and violent bumping again occurred. It could be seen at this point that the reaction mass must be agitated during this type of distillation. This run was discarded because some reaction mixture was ejected into the receiver flask. In run 6, the amount of water in the reaction mix was lowered by using a 50% NaOH solution. During vacuum distillation an agitator was used in the pot. The agitator aided the distillation and prevented bumping. In scaled-up runs 7 and 8 an air bleed was used to agitate the reaction mix during vacuum distillation. Fig. 2 shows the equipment used in these runs. Table 2 summarizes the results obtained using vacuum distillation.

Table 2

Results Obtained by Vacuum Distillation

Run	Strength of NaOH soln.	Yield	Chlorine analysis	Melting range
	%	%	%	°C.
5	16.25	-	-	-
6	50.00	-	0.96	57.5-61.5
7	50.0	67.3	0.29	55.2-59.9
8	50.0	45.9	0.23	53.5-59.5

The quality of the product produced by this procedure seems fairly good, but the trouble encountered during a vacuum distillation, the hot filtration (above the melting point of product), the length of time required to strip off the water, and the low yield of product eliminated this procedure from further consideration.

(c) Drying. Runs 9 and 10 were made using 50% NaOH solution to reduce the amount of water in the reaction mix. Salt precipitated during the reaction and was then filtered off. The filtrate was placed into an evaporating dish and dried overnight in an oven at 70°C. The dried product was filtered again to remove NaCl which had precipitated due to the removal of water.

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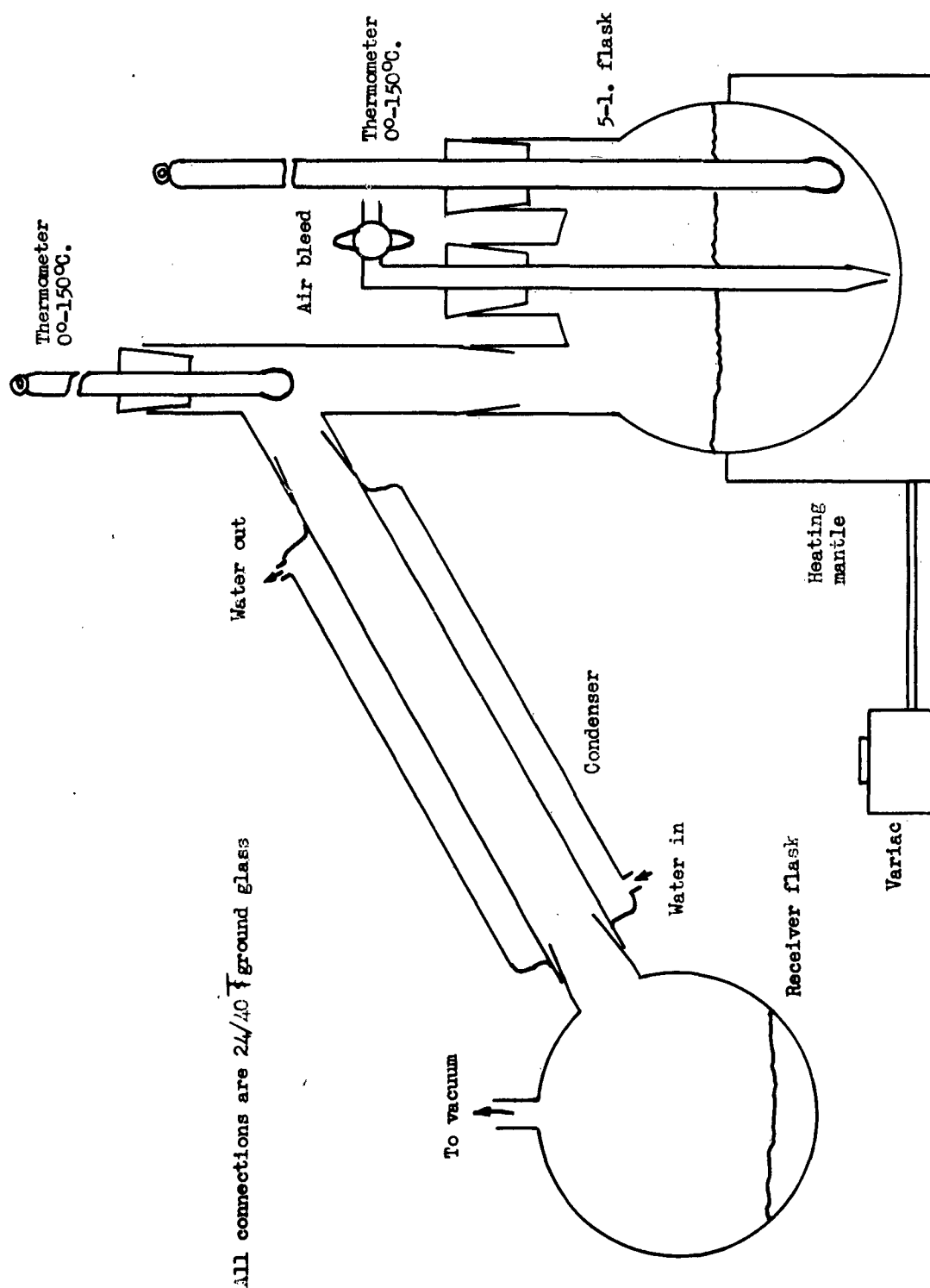


FIGURE 2
VACUUM DISTILLATION OF REACTION MDX

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Apparent yields on both runs were extremely high (122%), which indicated that water and NaCl were not completely removed by the drying operation. Table 3 gives the results of these runs.

Table 3

Purification by Oven Drying

Run	Apparent yield	Chlorine	Melting range
	%	%	°C.
9	122	1.16	55.5-60
10	122	1.21	41.5-48.5

(2) Extraction of Sesquiglycol.

(a) Extraction With Acetone. Several runs were made to see if acetone could be used to extract sesquiglycol from the reaction mix. In run 11, 200 g. of acetone was added to the reaction mass to extract the product. Two layers formed almost instantly, the acetone layer on top having a reddish color. The two layers were separated in a 1-liter separatory funnel, and the acetone was distilled from the glycol. This material melted over a range of 61.5° to 65°C. The chloride analysis was comparatively high at 6.2%, and only 85.7% of the theoretical yield was recovered.

Run 12 was made using a 50% NaOH solution to reduce the amount of water in the reaction mix. NaCl precipitated during the addition of ethylene dichloride. Acetone (300 ml.) was poured into the reaction flask and stirred vigorously. This mixture was poured into 200 ml. of acetone. The salt in the mixture settled out, but only one liquid phase was observed. The salt was filtered off and washed with 100 ml. of acetone, which was added to the filtrate. The solvent was distilled from the product layer, and the product was dried. The yield was 93.9% of theoretical, which contained 1.59% Cl and had a melting range of 52.5° to 60.5°C.

(b) Extraction With Methanol. The same procedure was followed in run 13 as in run 12, except that methanol was used as the extraction medium. During the distillation of the solvent from the product, it was noted that the glycol turned reddish brown, indicating decomposition, and work along this line was stopped.

(c) Extraction With Methylene Chloride. Table 4 lists the solubility of sesquiglycol and agent Q in various solvents (6). Although several solvents met the solubility requirements (e.g., chloroform and ethyl acetate), none, other than methylene chloride, met the boiling-

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point and density requirements. Methylene chloride was used because of its relatively low boiling point (40° to 41°C.) and its relatively high density of 1.336 g./ml. as compared with water. The boiling-point requirement was established to minimize the entrainment of Q with the solvent, while the density requirement was established to facilitate separation in the batch extraction of sesquiglycol from the reaction mix.

Table 4

Solubility of Sesquiglycol and Agent Q in Various Solvents at 30°C. (7)

Solvent	Solubility	
	Sesquiglycol	Agent Q
	g./l.	g./l.
Acetone	265.5	1,017
Benzene	7.3	1,198
Chloroform	95.7	1,775
Bis(2-chloroethyl) ether	83.8	-
Dimethyl formamide	450.1	-
Ethyl alcohol	241.0	43
Ethyl ether	15.0	-
Ethylene dichloride	46.0	-
Water	418.5	-
Ethyl acetate	87.3	863
Saturated brine	39.0	-
Dichloromethane	75.0	599.8
1,4-Dioxane	-	1,491
Carbon tetrachloride	-	456
Methanol	-	79

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Table 5

Summary of Runs Made to Isolate Sesquiglycol

Run number	Scale	Notebook number	Isolation procedure	Comments
1	1	SG-12	Cooling and filtration	Reaction mix solidified
2	1/10	SG-13	Settling and separating at 65°C.	Too much water and NaCl in oil layer
3	1/10	SG-56	Settling and separating at 65°C.	Too much water and NaCl in oil layer
4	1/10	SG-14	Atmospheric distillation of water and extraction with acetone	Decomposition or charring of product
5	1/10	SG-16	Vacuum distillation	Violent bumping during distillation
6	1/10	SG-22	50% NaOH and vacuum distillation	Procedure too involved for further work
7	1.5	SG-23	50% NaOH and vacuum distillation	Procedure too involved for further work
8	1.5	SG-24	50% NaOH and vacuum distillation	Procedure too involved for further work
9	1.5	SG-20	50% NaOH; product dried in oven to evaporate H ₂ O	Not all water removed by this method
10	1.5	SG-21	50% NaOH; product dried in oven to evaporate H ₂ O	Not all water removed by this method
11	1/10	SG-15	Extraction with 200 g. acetone	High salt in product
12	1/10	SG-17	50% NaOH; extraction 500 ml. acetone	Fairly good product; b.p. of solvent not low enough
13	1/10	SG-19	50% NaOH; extraction 500 ml. methanol	Decomposition of product
14-23	1	SG-25-34	Extracted with 2,000 ml. CH ₂ Cl ₂	Used for production
24-43	1	SG-35-55	Extracted with 3,000 ml. CH ₂ Cl ₂	Used for production
44-45	1/10	SG-57,59	Extracted with 597 ml. CH ₂ Cl ₂ at 35°C.	To determine split in batch extractor
46	1/10	SG-60	Extracted with 597 ml. CH ₂ Cl ₂ at 35°C.	Chlorinated directly
47-48	1/10	SG-18,58	Runs discarded because of operational mishaps	

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Beginning with run 24, the reaction mix, on completion of the reaction, was poured into 3,000 ml. of methylene chloride in a battery jar and stirred thoroughly. In runs 14 to 23, only 2,000 ml. of methylene chloride was used (see table 5, which summarizes the work to isolate sesquiglycol). On standing, two layers formed which were separated while the solutions were still hot (35° to 40°C.). The methylene chloride layer was put into a 5-l. flask and distilled batchwise (fig. 3). Distillation was continued until the pot temperature was approx. 90°C. Although this temperature is far above the boiling point of methylene chloride, not all of the solvent was removed. The product was poured into a flat pyrex dish and allowed to solidify. This solid was broken up with a spatula and ground in a "Fitz-Mill" to give a fine white powder.

The aqueous layer was allowed to cool slowly in a battery jar overnight, and the product which had precipitated was filtered on a 12-in. Büchner funnel, dissolved in methylene chloride, and added to the distilling flask.

(d) Extraction With Methylene Chloride to Give Chlorination Mixture. Reeves and Chiesa (6) developed a procedure for chlorinating a 12% sesquiglycol solution in methylene chloride. Work was undertaken to determine if a solution of this concentration could be obtained by extraction of the reaction mixture.

Runs 44 and 45 were prepared in the standard manner and, on completion of the reaction, were poured slowly into 597 ml. (797 g.) of methylene chloride solution. This volume of solvent would form a 12% solution if all the glycol were extracted. This mixture was shaken up in a 1-liter separatory funnel and allowed to come to equilibrium at 35°C. in a constant-temperature bath. The two layers were separated and analyzed. Results are shown in table 6.

Table 6

Analytical Results, Runs 44 and 45

Run	Aqueous layer		Solvent layer		
	Chlorine	Sulfur	Chlorine	Sulfur	Water (Karl Fischer)
	%	%	%	%	%
44	13.07	1.21	1.60	4.18	0.76
45	12.93	1.38	1.21	4.31	0.74

Ionic chlorine analyses indicated unrealistic amounts of salt in both layers. It was believed that this was due to some hydrolysis of methylene chloride occurring during the analyses. The sulfur analyses were also high.

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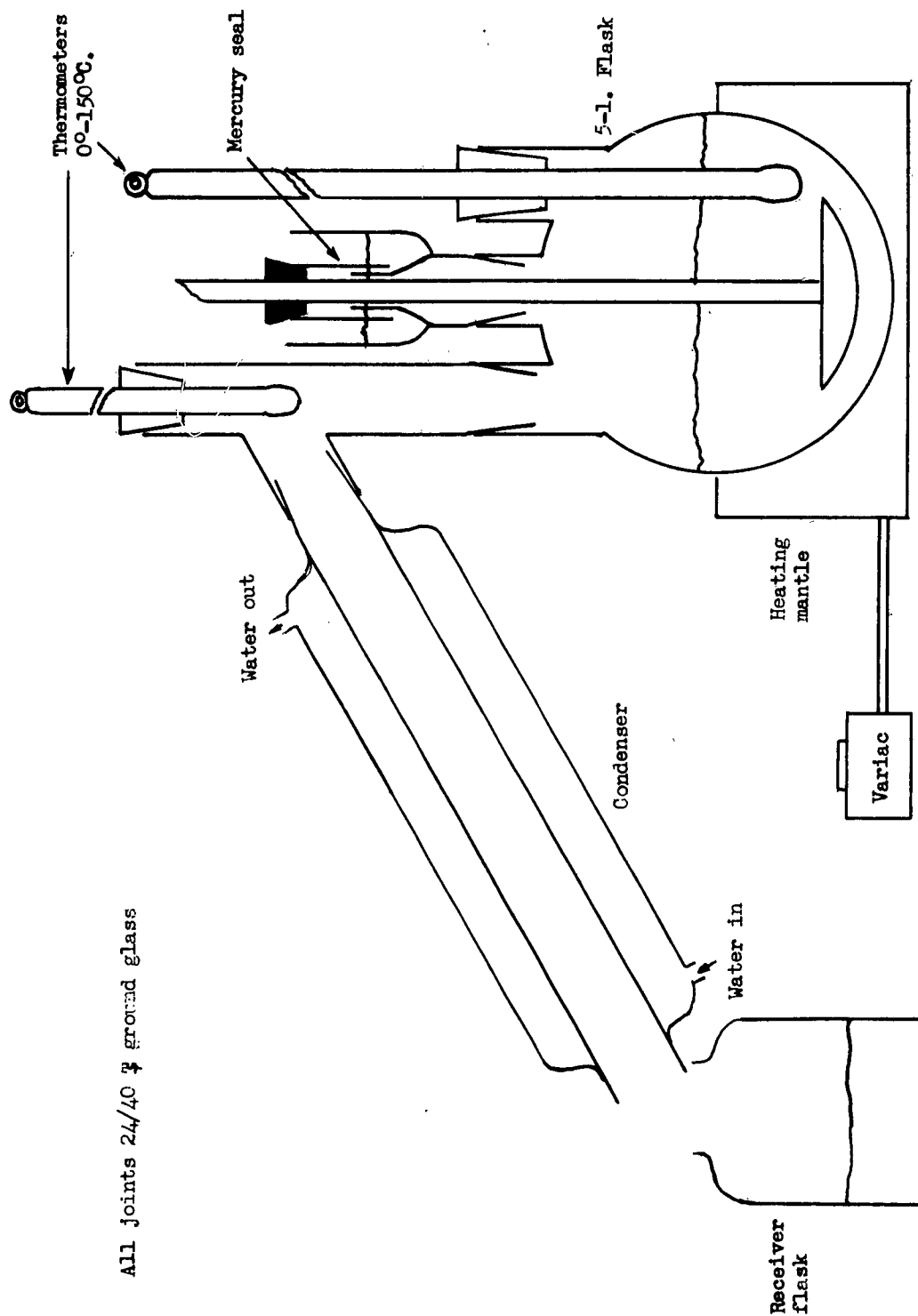


FIGURE 3
SOLVENT STRIPPING APPARATUS

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From the data in table 6 and the stream split (28% by weight goes to aqueous layer), an adjusted material balance on these runs was made. The amount of salt in the solvent layer was calculated by assuming that the salt was present in a saturated brine solution (26.3% NaCl) in the solvent. The amount of brine in the solvent layer was calculated from the water analysis. By then assuming that the reaction went to completion, the amount of salt in the aqueous layer was calculated by difference.

The sulfur analyses were high to some extent, and they were reduced proportionally to give a 100% yield of sesquiglycol. The remaining material balance can then be calculated by difference. Table 7 gives a complete adjusted material balance for the two runs made.

Table 7
Adjusted Material Balance

Component	Solvent layer		Water layer	
	g.	%	g.	%
NaCl	2.4	0.27	67.7	19.29
Sesquiglycol	97.8	10.85	11.5	3.28
Water	6.8	0.75	264.8	75.60
Solvent	794.4	88.2	2.6	0.74
Unaccountable	-	-	4.4	-
	<hr/> 901.4	<hr/> 100.07	<hr/> 351.0	<hr/> 98.91

Run 46 was prepared in the same manner, and the solvent layer was chlorinated directly with phosphorus trichloride to form agent Q.

(3) Summary. By extracting the reaction mix with methylene chloride, 62.4 lb. of sesquiglycol has been produced. Table 8 gives the results of these runs.

Yields on runs varied because the precipitate from the water layer was not added to each run individually. In some cases, two and three water layers were filtered at one time and added to a batch. The average yield per run was 86.4%. This figure is low when compared with yields of up to 96% obtained by Adams and Marvel (4). This is probably explained by the fact that no attempt other than the filtration mentioned above was made to recover glycol from the water layer.

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Table 8
Preparation of Sasquiglycol in Chemical Process Laboratory

Run	Yield	Analysis		Melting range	Melting range, dry
		Chlorine	Volatile matter		
	g.	%	%	°C.	°C.
14	956	0.23	-	-	-
15	852	-	-	-	-
16	694	-	-	-	-
17	983	-	-	-	-
18	1,003	0.96	-	-	-
19	1,086	0.67	-	-	-
20	790	1.03	-	-	-
21	878	1.84	4.5	-	-
22	790	1.37	1.5	49.0-58.5	62.0-65.0
23	1,092	2.30	6.5	56.0-63.5	62.0-66.0
24	1,181	-	6.5	54.0-57.0	65.0-67.0
25	1,343	-	9.2	57.0-60.0	64.0-66.5
26	1,043	-	10.0	48.5-52.0	61.0-62.0
27	1,048	-	3.5	47.2-52.0	62.0-64.2
28	1,016	-	3.4	-	-
29	1,075	-	1.8	53.0-59.0	63.0-65.0
30	1,000	-	3.5	57.0-61.0	62.0-65.0
31	1,027	-	7.5	54.0-61.5	61.0-67.0
32	910	-	4.0	55.0-59.0	63.0-65.0
33	986	-	6.7	51.0-54.0	64.0-66.0
34	1,097	-	8.5	57.0-61.0	62.0-65.0
35	941	-	6.0	50.0-56.0	62.0-65.0
36	1,202	-	3.1	-	-
37	1,192	-	2.9	-	-
38	1,000*	-	6.4	-	-
39	1,015	-	-	-	-
40	1,051	-	-	-	-
41	1,158	-	-	-	-
42	931	-	-	-	-
43	1,192	-	-	-	-
Average	1,018	1.2	5.3		

*Assumed, as no yield was determined.

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The average content of chloride was 1.2% and of volatile matter was 5.3%, as determined on a Cenco moisture meter. The volatile matter varied widely with each batch. This is probably due to differences in solvent removal. No further attempt was made to dry the product, as it was assumed that all the volatile matter was methylene chloride.

Melting ranges determined before drying in the moisture meter were erratic and varied widely. After drying, the melting ranges were all between 61° and 67°C. with little variation between batches. A Thiele melting-point apparatus was used to determine these melting ranges.

3. Distribution Coefficient of Sesquiglycol.

Laboratory work was performed to determine the distribution of sesquiglycol between methylene chloride and water or brine solutions at room temperature (18°C.) and at 35°C. The composition of the solutions tested is given in table 9.

Table 9

Composition of Solutions

Solution	A	B	C
Density	1.063	1.149	1.000
NaCl, % by wt.	8.6	21.1	0
Sesquiglycol, % by wt.	4.96	2.96	4.76

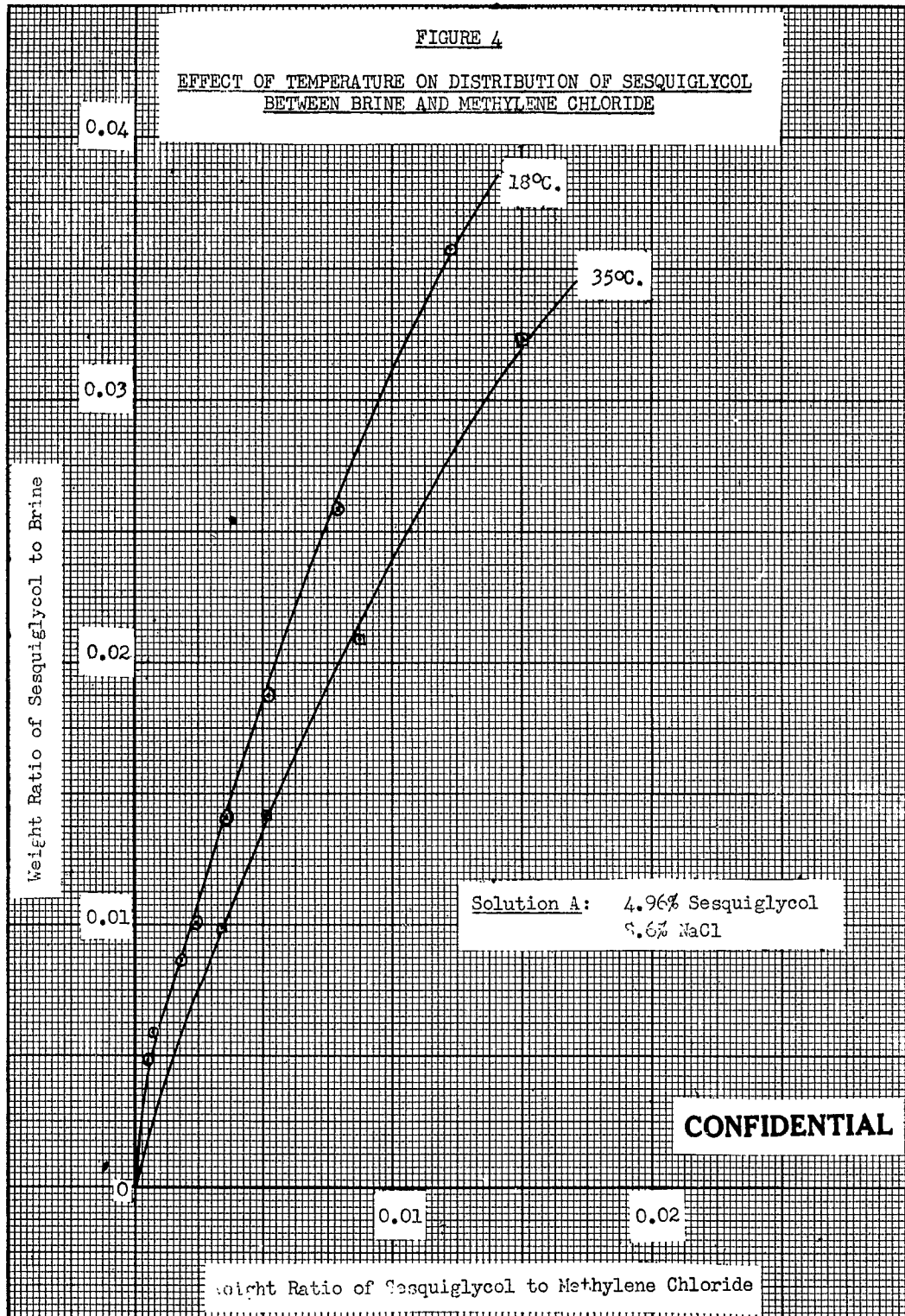
A 100-ml. quantity of each solution was shaken well with 100 ml. of methylene chloride in a separatory funnel, and the solvent (lower) layer was drawn off into a clean, tared 200-ml. tall beaker. The beaker was dried to constant weight in a drier at 40°C. Assuming that the weight gain was due to extracted sesquiglycol (no salt extracted), equilibrium data were calculated.

To study the effect of temperature, the solution containing 4.96% by wt. of sesquiglycol and 8.6% by wt. of salt (A) was extracted with methylene chloride at both 18° and 35°C. Fig. 4 is a plot of the equilibrium curve at the two temperatures. Increasing the temperature increases the distribution coefficient.

Inorganic salts are known to change the solubility of organic material in water. The effect of salt on the distribution coefficient of sesquiglycol between water and methylene chloride was studied. Data are given in fig. 5

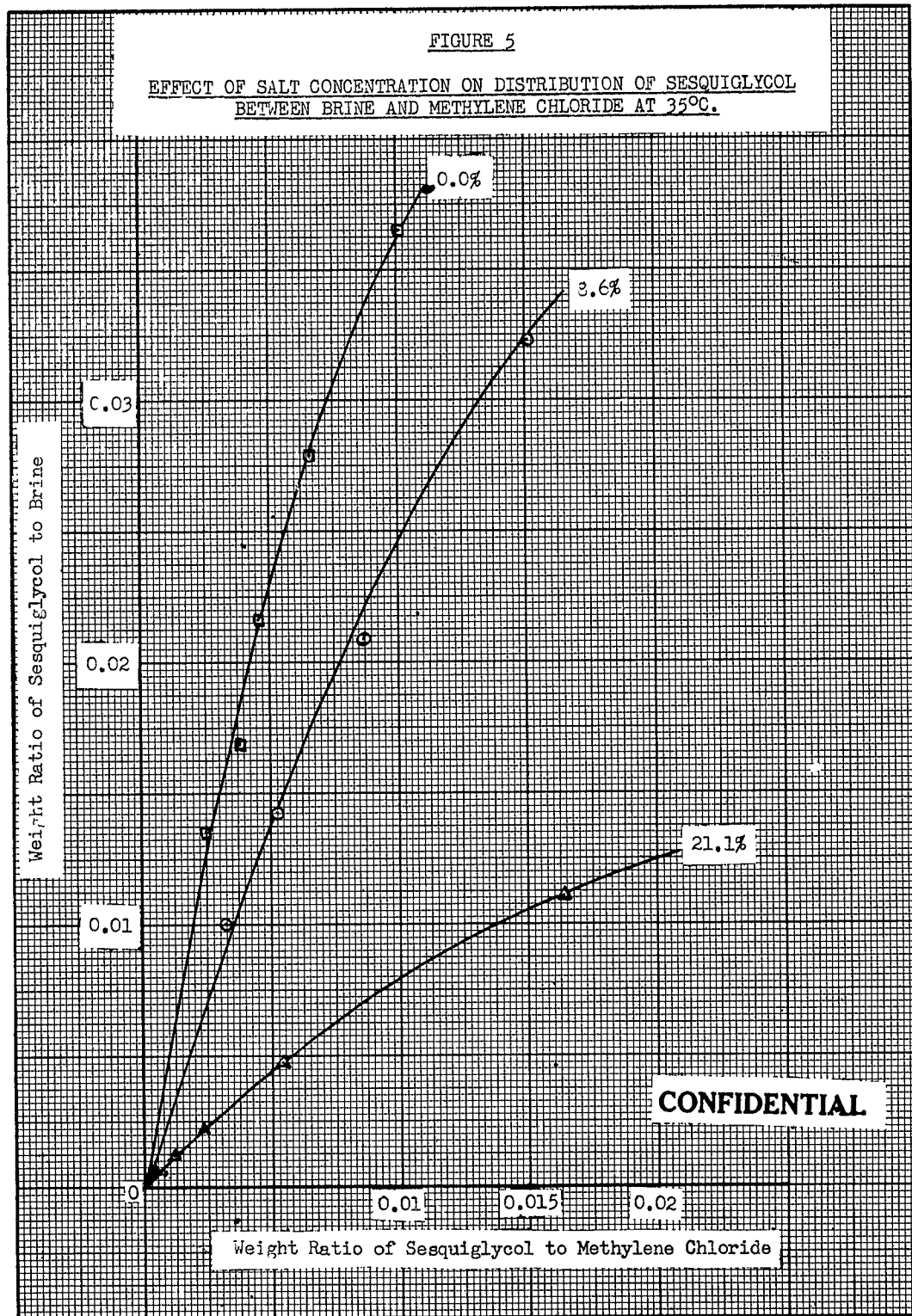
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The equilibrium shifts toward the solvent layer as the concentration of salt increases. Swabb and Morgan (8) have applied the Setschenow equation to the effect of inorganic salts on the distribution coefficient. For this purpose, the Setschenow equation is:

$$\ln \frac{C_o}{C} = ku$$

where C = concentration of nonelectrolyte in the aqueous phase

C_o = concentration of the nonelectrolyte in aqueous solution (u=0)
in equilibrium with the same solvent phase as C, above

u = concentration of electrolyte in aqueous phase

k = constant

This equation can be applied to evaluate the salting-out effect of the sodium chloride on an equilibrium solution of water, sesquiglycol, and methylene chloride.

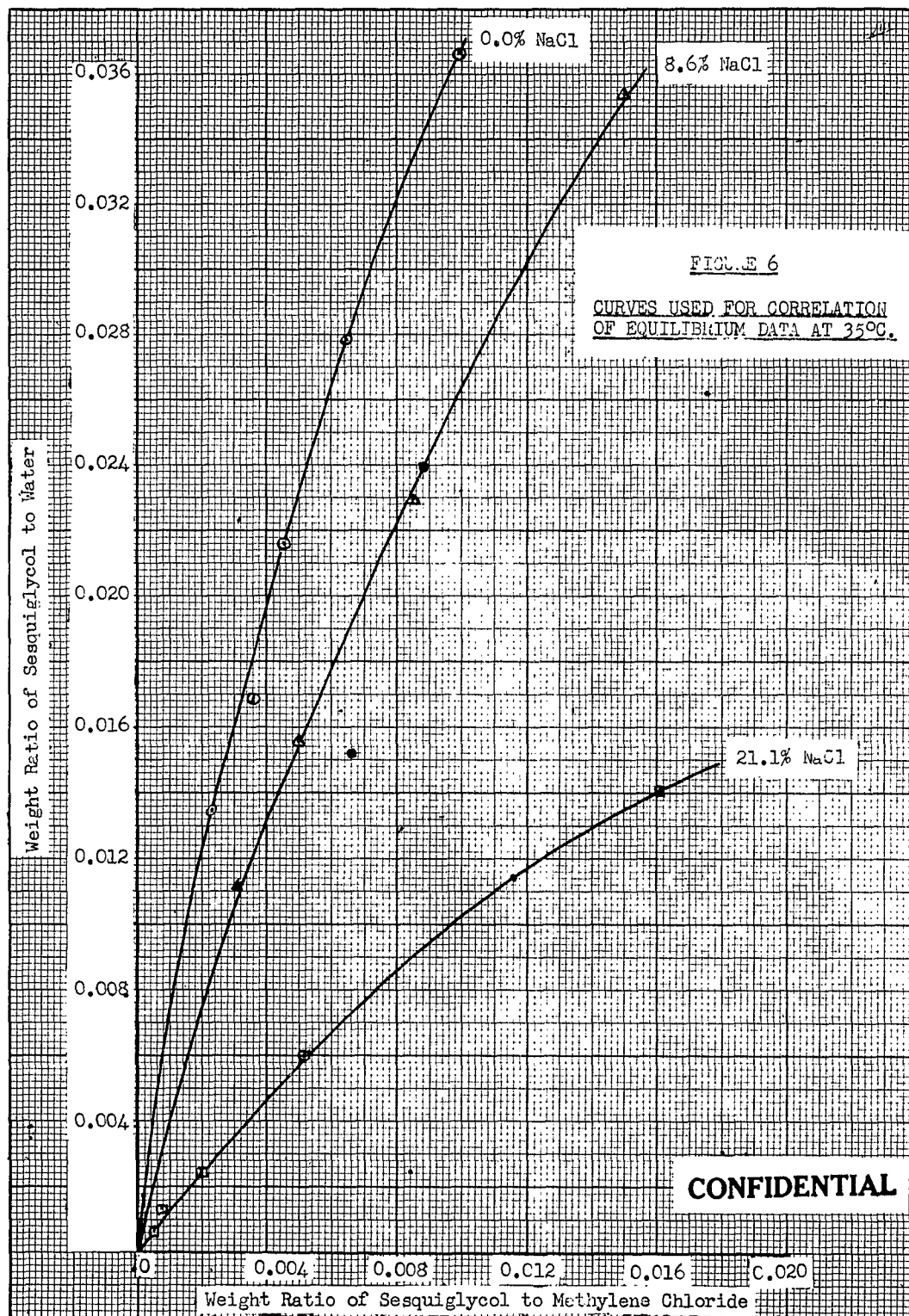
From the equilibrium curves (fig. 5) a plot of the weight ratio of sesquiglycol to methylene chloride versus the weight ratio of sesquiglycol to water can be constructed (fig. 6). From this plot, values of k to fit the above equation were calculated. The data obtained in the laboratory did not fit the Setschenow equation because this equation holds only for low salt concentrations. The data that were obtained were fitted into the empirical equation:

$$\ln \frac{C_o}{C} = 13.5 u^{1.5}$$

Table 10 summarizes the extraction data.

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Table 10

Tabulation of Extraction Data

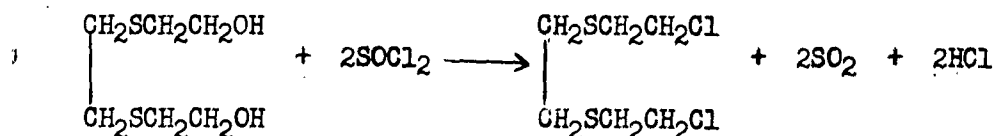
Extraction	Amount of sesquiglycol extracted			
	Soln. A		Soln. B at 35°C.*	Soln. C at 35°C.
	At 18°C.	At 35°C.*		
	g.	g.	g.	g.
1	1.639	2.000	2.162	1.337
2	1.028	1.144	0.714	0.863
3	0.701	0.687	0.280	0.621
4	0.472	0.422	0.124	0.497
5	0.320	-	0.074	0.324
6	0.229	-	-	-
7	0.153	-	-	-
8	0.098	-	-	-
9	0.090	-	-	-
10	0.044	-	-	-

*Average of two determinations.

C. Preparation of 1,2-Bis(2-chloroethylthio)ethane or Agent Q.

1. Chlorination With Thionyl Chloride.

The hydroxy compound was converted to Q by chlorination with thionyl chloride in ethyl ether solution. The reaction is as follows:



Agent Q was made in the Process Laboratory in a 10-gal. jacketed reactor, following the procedure outlined in CRLR 396 (1).

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Approx. 14,700 cc. of anhydrous ethyl ether was charged to the reactor, which was equipped with a reflux condenser cooled with CaCl_2 brine at -20°C . Then 5,900 g. of thionyl chloride, redistilled with 1% to 2% acetone to remove sulfuryl chloride (see appendix), was placed in the reactor, and 4,540 g. of sesquiglycol was added over 2.5 hr., with agitation. The reactor temperature was maintained at 15° to 20°C . After the addition was complete, an additional 1.5 hr. of agitation was allowed for the completion of the reaction. The ethyl ether was then distilled and recovered, the last fraction being removed under reduced pressure.

The product was completely degassed under 100 mm. vacuum and heated to 50°C . The Q was then melted (50° to 60°C .) at atmospheric pressure, dropped into pyrex battery jars, and poured into pyrex pans to solidify. After the material had solidified, it was broken up, sampled, and packed in wide-mouth quart jars.

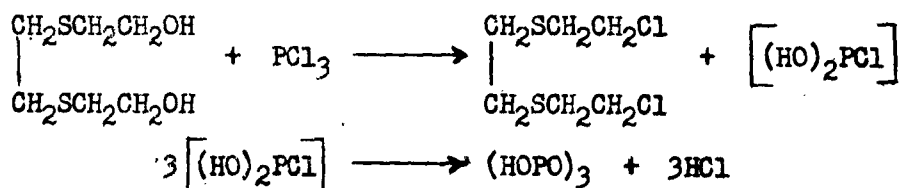
Using this procedure 17 lb. of Q was manufactured in two runs. The product was tan and sticky. It was 41% to 65% pure and melted at a higher temperature than pure Q. Results are listed in table 11.

Although this low-purity Q was unacceptable, its purity could be increased by washing with 95% ethanol. The reason for the low purity was believed caused by the presence of sulfuryl chloride in the thionyl chloride (chlorinating agent) and the retention of sulfur dioxide and hydrochloric acid in the reaction mixture.

Since it was imperative to manufacture high-purity Q with as little handling as possible, reworking was considered impractical. Also, sesquiglycol suspended in methylene chloride had been chlorinated successfully with phosphorus trichloride on a laboratory scale (6).

2. Chlorination With Phosphorus Trichloride.

The chlorination of sesquiglycol with phosphorus trichloride is assumed to proceed as follows:

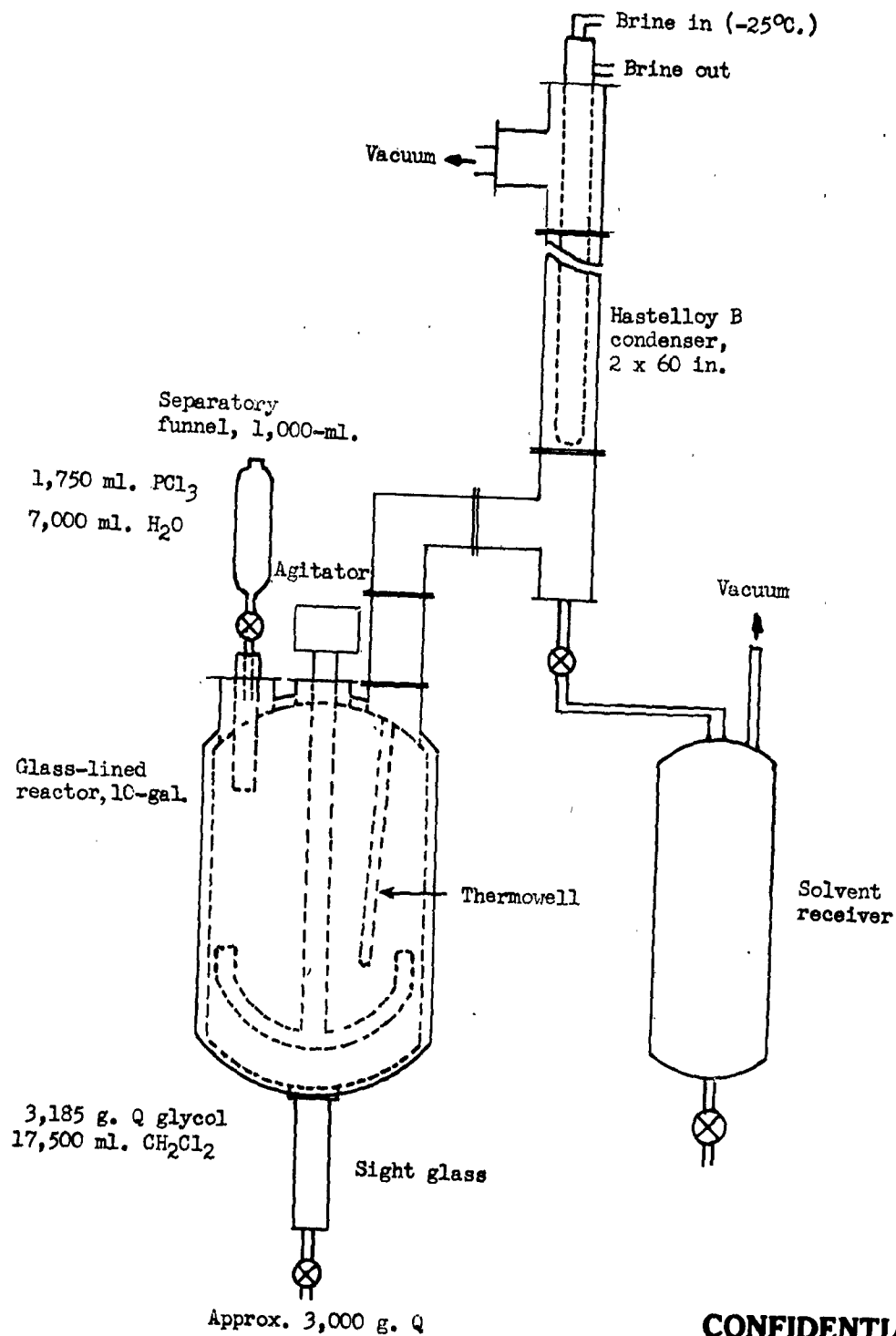


A 10-gal. jacketed, glass-lined reactor with a condenser and a PCl_3 -water feed (fig. 7) was used for the chlorination reaction. Approx. 30 lb. of Q was made by the following procedure:

To the methylene chloride (17,500 ml.) in the reactor 3,185 g. of solid, finely ground Q glycol was added, with agitation, over a 15-min. period. A suspension was formed during the course of this addition.

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FIGURE 7

CHLORINATION OF SESQUIGLYCOL WITH PHOSPHORUS TRICHLORIDE

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Table 11

Manufacture of Q

Run no.	Glycol	Chlorinating agent	Solvent	Product	Theoretical yield (a)	Melting point	Purity
	g.			g.	%	°C.	%
PL-Q-6	3,019	SOCl ₂	(C ₂ H ₅) ₂ O	3,442	95	63-67.5	41
PL-Q-7	4,000	SOCl ₂	(C ₂ H ₅) ₂ O	4,241	88	44-59	65
PL-Q-8	2,730	PCl ₃	CH ₂ Cl ₂	3,005	92	44-56	91
PL-Q-9	3,640	PCl ₃	CH ₂ Cl ₂	3,561	81	43-50	89
PL-Q-10	3,185	PCl ₃	CH ₂ Cl ₂ (b)	2,985	83	46-52	80
PL-Q-11	3,185	PCl ₃	CH ₂ Cl ₂ (b)	2,200	57	49-53	79
PL-Q-12	3,185	PCl ₃	CH ₂ Cl ₂ (b)	2,310	60	48-56	86
Glycol run 46 (c)	89.9	PCl ₃	CH ₂ Cl ₂	93.7	87	47.5-52.5	95.3

(a) Yield considered 100% Q.

(b) Recovered solvent used.

(c) Chlorination by Chiesa in laboratory.

Phosphorus trichloride (1,750 ml.) was added to the reactor, dropwise, at first, over a period of 30 to 60 min. A small amount of heat was evolved during the reaction, but the temperature remained below 35°C. and a moderate reflux of methylene chloride was maintained. Agitation was continued for 1/2 hr. after the addition of phosphorus trichloride. At the completion of the reaction, two layers were present in the reactor, an upper, fairly clear solution and a lower, heavy viscous syrup.

To hydrolyze the excess phosphorus trichloride and to dilute the viscous by-product layer, 7,000 ml. of water was added carefully, with agitation. The methylene chloride reflux rate was used to determine the water addition rate (as the temperature-control criterion) during the hydrolysis. Approx. 350 ml. of water was required for the hydrolysis of the excess PCl₃, and the remaining 95% (6,650 ml.) was used to wash the product and to dilute the heavy by-product layer. The two layers were allowed to separate. At this point

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the layer of Q in methylene chloride was heavier than the layer of water and by-product. The bottom layer was drawn off slowly through a 12 by 3-in. sight glass into 4-l. glass-stoppered bottles to be recharged into the reactor. The water layer was then drawn off into a container and detoxified with CCl_2 .

The Q solution was recharged to the reactor, and methylene chloride was stripped off and recovered, the last fraction being removed under a reduced pressure of 100 mm.

The product was degassed under vacuum below 50°C . The Q was then melted at atmospheric pressure (55° to 60°C .) and collected in pyrex battery jars. After solidification the product was broken up, sampled, and packed in wide-mouth quart jars. The Q was white and brittle.

The results with the PCl_3 chlorination process are shown in table 11.

In run PL-Q-8, the procedure developed by Reeves, Chiesa, and Vail (6) was scaled up by a factor of 20, adapting the procedure to the equipment available. Q of high purity and good physical characteristics (brittle and light colored) was produced in this run.

It was desired to increase the yield to utilize the entire 10-gal. reactor; therefore, the laboratory procedure was scaled up by a factor of 40 in run PL-Q-9. Good quality Q, similar to the previous run, was produced. Due to the large volume of methylene chloride used (20,000 ml.), it was difficult to distill the solvent without bumping or boilups in the condenser and receiver. This resulted in a lower yield.

In subsequent runs, the laboratory procedure was scaled up by a factor of 35. Recovered solvent was used, which may be responsible for the lower yield and purity. This indicates that the HCl should probably be removed completely from the recovered solvent prior to re-use.

In run 46, sesquiglycol extracted from the reaction mixture (table 5) was chlorinated directly in the solvent using 1:1 molar ratio of phosphorus trichloride. An 87% yield of an acceptable, high-purity product (95.3%) resulted. This illustrated the feasibility of a semicontinuous process incorporating the direct chlorination of the extraction mixture from the Adams-Marvel condensation (4).

This work demonstrates that high-quality Q can be produced by chlorinating sesquiglycol with phosphorus trichloride, using methylene chloride as a carrier for the glycol.

IV. DISCUSSION OF PROPOSED SEMICONTINUOUS PROCESS.

After developing a method for directly chlorinating sesquiglycol in methylene chloride with phosphorus trichloride, the development of a semicontinuous process was undertaken.

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The reaction mixture from the condensation was extracted with methylene chloride at 35°C. (using a weight ratio of solvent to glycol of 7.3 to 1). A solvent layer containing 10.85% glycol was obtained. This stream could be chlorinated without further processing.

However, about 12% of the sesquiglycol produced remains in the aqueous phase on separation. To operate this process economically, this material must be recovered. This can be done continuously in several types of liquid-liquid extraction apparatus.

Fig. 8 is a proposed flow diagram of the process giving a material balance based on 2.5 lb. moles of sesquiglycol produced (100% yield). The equipment required and some operating conditions are also given.

The extraction-column material balance is based on a 98% recovery of sesquiglycol. Owing to the large amount of solvent which is used, the extract coming from the column is extremely dilute (1.4% sesquiglycol), and it is possible to recycle this stream and use it in the batch extraction of the reaction mix. The raffinate stream, containing only 0.0725% of sesquiglycol and no toxic matter, can then be discarded.

By recycling the extract stream to the batch extractor, the only loss of sesquiglycol is in the raffinate. The 10.85% stream of sesquiglycol can then be put into a reactor and chlorinated directly with phosphorus trichloride. On completion of this step, a water wash to hydrolyze excess chlorinating agent is required. This water wash should also remove any salt which has been carried over from the condensation reaction. The product from the chlorination step, agent Q, is extremely soluble in methylene chloride (table 4). The aqueous phase can then be separated, decontaminated by chlorination, and discarded at this point.

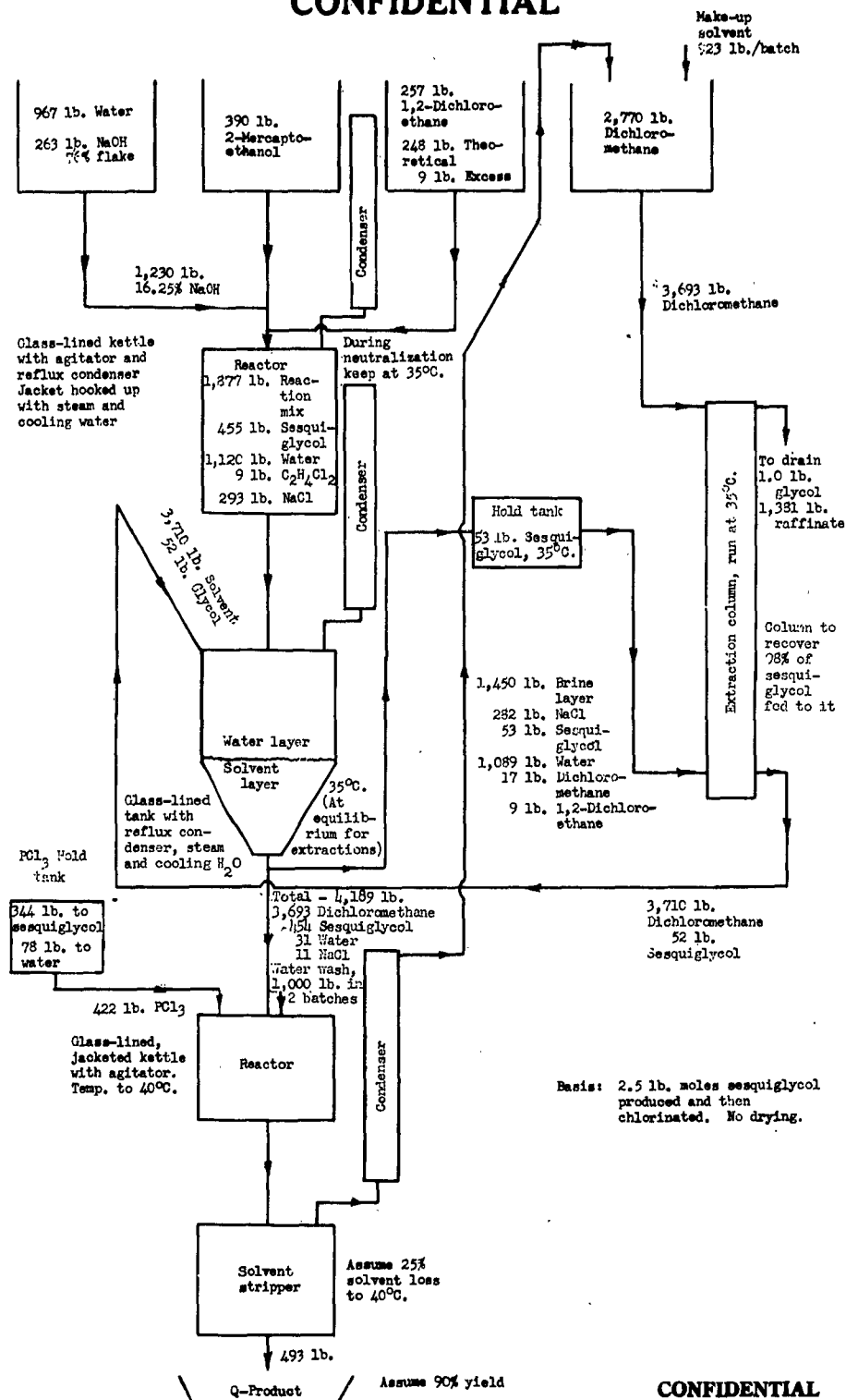
The solvent layer containing the product is sent to a solvent stripper, which removes the solvent. Methylene chloride boils at 40° to 41°C., which is below the melting point of agent Q (54°C.). The solvent can be recycled to the extraction column while the agent can be melted and cast.

In the flow diagram, it should be noted that the solvent-sesquiglycol stream contained 0.75% water. Though water does not have any apparent detrimental effect on the chlorination reaction, it will hydrolyze some of the chlorinating agent (PCl_3), thus requiring the use of excess material. To reduce the amount required, water can be removed from the process stream by a drying agent. Anhydrous sodium sulfate was considered for possible use in this capacity.

Two types of equipment considered for this operation are a packed tower and a tank with agitator in conjunction with a rotary filter. This equipment would add considerably to the initial capital cost of the plant. Calculations, based on the price of raw materials, were made comparing the cost of agent Q with sodium sulfate as a drying agent and

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FIGURE 8
SEMICONTINUOUS PROCESS, FLOW DIAGRAM

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without the use of the drier. On this basis, without considering capital investment, labor, and maintenance, the cost differential was negligible. Drying of the glycol-solvent stream was eliminated from further consideration because of these economic factors. Therefore, no experimental work was done on this problem.

In calculating the material balance (table 12) of this proposed process, it was assumed that 100% yield could be attained in the condensation. This figure is believed to be reasonable, as yields to 96% were attained in the laboratory by Adams and Marvel. A yield of 90% was assumed in the chlorination step, and yields of this type were attained. Equilibrium considerations in the batch extractor are based on the adjusted material balances on runs 44 and 45. Work to firm up data on the batch extraction unit, particularly since recycle solvent was not used in the laboratory, should be undertaken. The type of continuous extraction equipment to be used should also be investigated.

In the chlorination step, the ratio of chlorinating agent to sesquiglycol will have to be determined. A method of indicating the end point of the chlorination should be devised. Decontamination of the aqueous layer is another problem to be taken into consideration.

V. CONCLUSIONS.

Agent Q can be prepared in high purity and with high yields by using phosphorus trichloride to chlorinate a suspension of sesquiglycol in methylene chloride. A process to manufacture this agent semicontinuously has been developed so that no intermediate purification of sesquiglycol is required.

VI. RECOMMENDATIONS.

It is recommended, if any future interest arises in this CW agent, that the process, as discussed in this report, be considered for pilot-plant operation.

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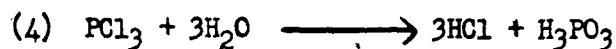
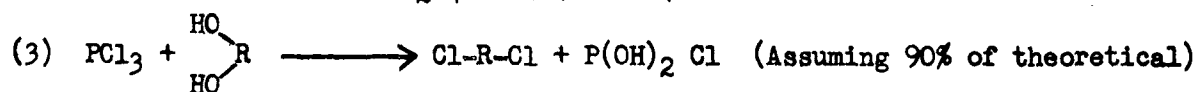
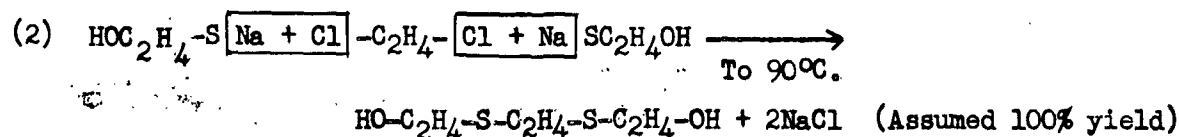
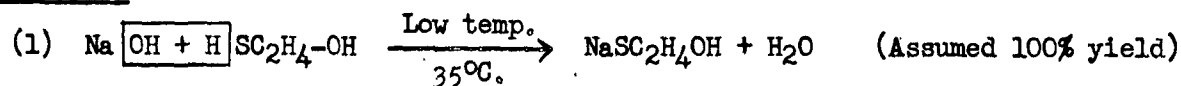
Table 12

Material Balance* - Proposed Process**

Material	Mol. wt.	Density	Amt.		Cost per pound	Product	Cost per batch
		g./ml.	lb. moles	lb.	\$	lb.	\$
Water	18.0	1.00	57.3	967	-	1030 + 90	-
NaOH (76% flake)	40.0	-	5	263	0.0500	-	13
2-Mercaptoethanol	78.0	-	5	390	1.523	-	594
1,2-Dichloroethane	99.0	-	2.6	257	0.1225	9	31
Dichloromethane	85.0	1.336	-	3,710	0.14	923	130
Phosphorus trichloride	137.4	1.574	2.5	422	0.12	-	51
NaSC ₂ H ₄ OH	100	-	-	-	-	500	-
Sesquiglycol	182	-	2.5	-	-	455	-
Q	219	-	2.5	-	-	493	-
NaCl	58.5	-	5	-	-	293	-
							819

*Material balance on 2.5 lb. moles glycol produced.

****Reactions:**



Cost: $\frac{819}{493} = 1.67$ (Based only on raw materials)

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APPENDIX

PURIFICATION OF THIONYL CHLORIDE

Thionyl chloride was purified following the method as outlined in British Patent No. 538,028 and CRLR 396. This includes the distillation of the crude thionyl chloride over 1% to 3% lower aliphatic ketone.

Six liters of crude thionyl chloride and 720 ml. of acetone were charged to a 10-gal. vessel equipped with a 4-ft. column, a cold-water reflux condenser, and a reflux splitter (fig. 9). The charge was distilled at atmospheric pressure, and the product was taken off at 78°C. A nitrogen blanket was maintained above the glass product-storage receivers to exclude oxygen and prevent discoloration. The distilled thionyl chloride was practically colorless as opposed to the orange-yellow color of the crude charge. No attempt was made to shield the receivers from light, however, and the material did discolor on standing for several days.

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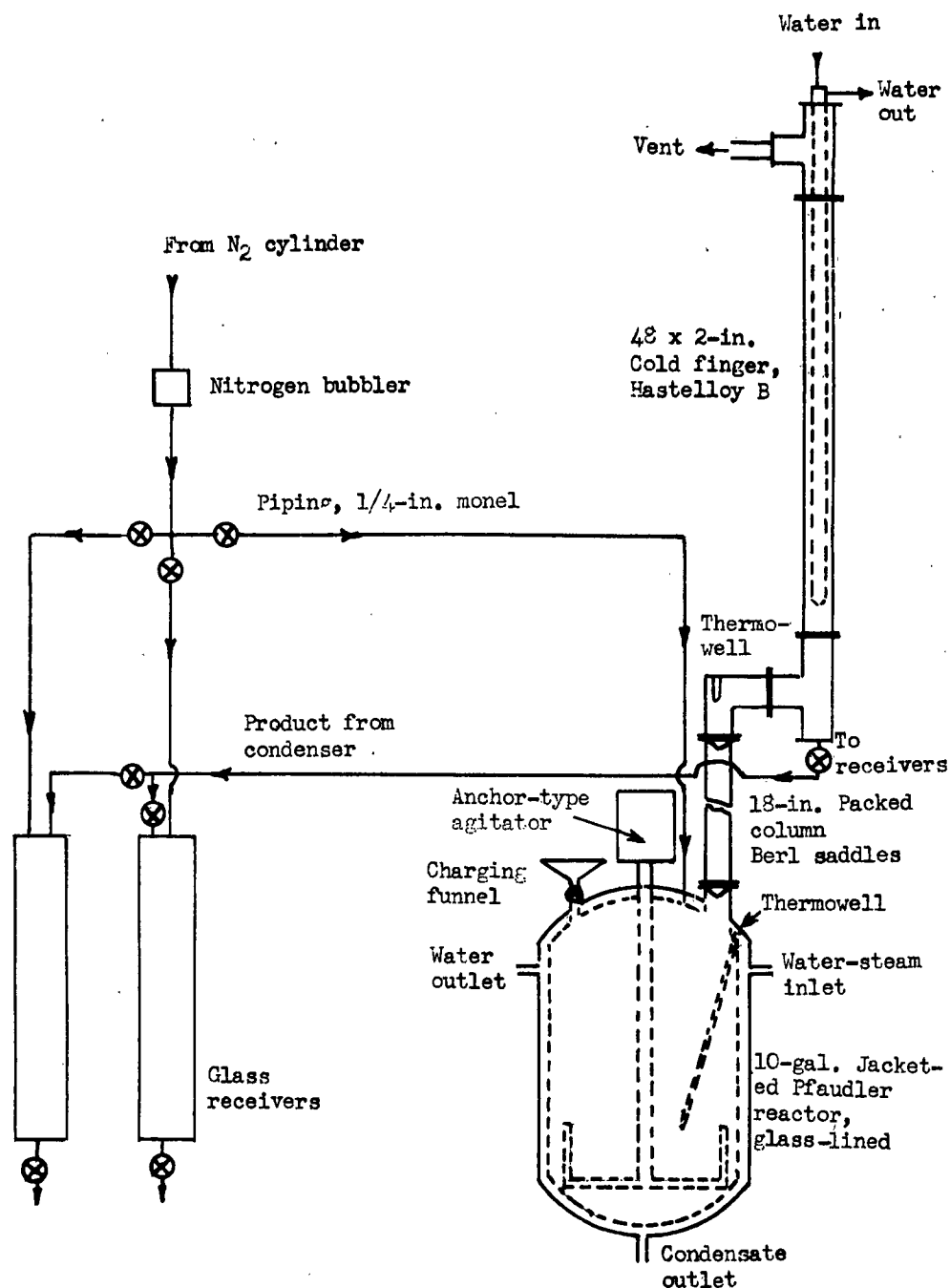


FIGURE 9

THIONYL CHLORIDE STILL

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